Syntheses and Properties of Bimetallic Chromophore-Quencher Assemblies Containing Ruthenium(II) and Rhenium(I) Centers

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We have prepared a family of six new bimetallic complexes containing electron-donating *trans*-{$Ru^{II}Cl(pdma)_2$}$^+$ [pdma = 1,2-phenylenebis(dimethylarsine)] centers linked to *trans*-[Ru^{II}Cl(pdma)(2,2′-bpy)(NO)] (bpy = bipyridyl) or *fac*-{$Re^{I}(biq)(CO)_3$}$^+$-based (biq = 2,2′-biquinolinyl) electron acceptors. The extended bridging units are based on 4,4′-bpy or bpe [*E*-1,2-bis(4-pyridyl)ethylene] ligands, and these assemblies are designed to display long-lived photoinduced charge-separated states. A number of new monometallic precursor complexes have also been synthesized and fully characterized. The electronic absorption spectra of the bimetallic species are dominated by intense, visible d(Ru^{II}) → π^*(4,4′-bpy/bpe) metal-to-ligand charge-transfer (MLCT) bands and d(Re^{I}) → π^*(biq) absorptions in the near-UV region. Cyclic voltammetric studies show both metal-based oxidation and ligand-based reduction processes and provide evidence that these assemblies contain thermodynamic driving forces for charge separation. Single-crystal X-ray structures have been determined for the monometallic complex salts *fac*-[Re^{I}(biq)(CO)$_3$(MeCN)]CF_3SO_3·$CHCl_3$, *fac*-[Re^{I}(biq)(CO)$_3$(4-$BrCH_2C_5H_4N$)]PF_6, *fac*-[Re^{I}(biq)(CO)$_3$(4-$HCO_2CH_2C_5H_4N$)]PF_6·Me_2CO, *fac*-[Re^{I}(biq)(CO)$_3$(ISNE)]CF_3SO_3 (ISNE = ethylisonicotinate), and *fac*-[Re^{I}(biq)(CO)$_3$($NC_5H_4CO_2$)]$_2$·HPF_6·3MeCN. Ultrafast time-resolved infrared and Raman spectroscopic measurements will be employed to investigate the photoexcitation properties of the bimetallic species and of monometallic reference complexes.

Introduction

Recent years have witnessed much interest in so-called photochemical molecular devices, which may find uses in emerging technologies such as artificial photosynthesis.[1] Within this field, a topic of particular importance is the creation and study of molecular assemblies capable of undergoing photoinduced charge separation (PICS) to produce long-lived charge-separated excited states.[2] Fullerene derivatives have proved popular as electron-accepting units in such systems; an especially long PICS lifetime has been achieved recently in a Zn^{II}-(chlorin)−C_{60} dyad (120 s at −150 °C in benzonitrile),[3] and the longest room-temperature lifetime (1.1 ms in benzonitrile) has been found in a diphenylaminopolyene−C_{60} dyad.[4] Organotransition metal complexes have historically played a prominant role in PICS studies due to the attractive features of metal-to-ligand charge-transfer (MLCT) chromophores, particularly Ru^{II}, Os^{II}, and Re^{I} polypyridyl species.[5] Studies with various chromophore-quencher (CQ) complexes containing electron donor (D) and/or acceptor (A) groups have revealed that a number of factors can influence PICS lifetimes. Since a pioneering report by Danielson et al.,[6] systems based on the archetypal MLCT chromophore [Ru^{II}(2,2′-bpy)$_3$]$^{2+}$ (bpy = bipyridyl) have been well studied, but are complicated by isomerism and their multichromophoric nature.[7] Nevertheless,

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permanent PICS has been achieved by using a zeolite-entrapped $[Ru^{II}(2,2'\text{-bpy})_3]^{2+}$ derivative with a diquat A unit,[8] and this approach has been extended to potentially useful membrane-based systems.[9]

The design of potentially useful CQ complexes requires optimization of both electronic and stereochemical properties, and the emphasis on the latter aspect has increased in recent investigations.[10] Given the presence of a MLCT chromophore with a sufficiently long excited-state lifetime and attached D and A groups, further desirable features can be summarized as follows: (i) a large and well-defined D−A separation that can be varied; (ii) selective and directional MLCT excitation; (iii) the presence of a spectroscopic reporter unit to allow probing of the formation and decay of PICS; (iv) high photochemical stability. We have previously prepared the complexes *trans*-$[Ru^{II}Cl(pdma)_2L^A]^{2+}$ [pdma = 1,2-phenylenebis(dimethylarsine); L^A = *N*-methyl-4,4′-bipyridinium (MeQ^+) or *N*-methyl-4-[*E*-2-(4-pyridyl)ethenyl]pyridinium ($Mebpe^+$)], which display intense $Ru^{II} \rightarrow L^A$ MLCT absorptions with λ_{max} values of ca. 490 nm in acetonitrile.[11,12] Replacement of the *N*-methyl groups in these complexes with separate A units affords CQ triad systems with well-separated end groups. As terminal A units we have chosen to use derivatives of the complexes *trans*-$[Ru^{II}Cl(pdma)(2,2'\text{-bpy})(NO)]^{2+}$ [13] and *fac*-$[Re^I(biq)(CO)_3L]^+$ (biq = 2,2′-biquinolinyl, L = a pyridyl ligand).[14] The reasons for choosing these units are (i) they are optically transparent around 490 nm, absorbing only to higher energy in the near UV;[13,14] (ii) both display redox potentials that indicate that they should be able to function as secondary electron acceptors from a MeQ^+ or $Mebpe^+$ unit;[13,14] and (iii) the presence of nitrosyl or carbonyl ligands with strong infrared absorptions will allow monitoring of photoexcitation properties via time-resolved infrared (TRIR) spectroscopy.[15] A particularly relevant report has appeared very recently from Gabrielsson et al. that describes ultrafast PICS in dyad systems comprising a Mg^{II} or Zn^{II} *meso*-tetraphenylporphyrin D chromophore connected via an amide linkage to a *fac*-$[Re^I(2,2'\text{-bpy})(CO)_3(pic)]^+$ (pic = 3-picoline) A unit.[16]

Experimental Section

Materials and Procedures. All reactions, except those involving thionyl bromide, were performed under an Ar atmosphere and in Ar-purged solvents. All chromatographic purifications involving complex salts were performed in the dark. The compound pdma was obtained from Dr G. Reid, University of Southampton. The compounds *fac*-$Ru^{II}Cl_3(pdma)(NO)$,[17] *trans*-$[Ru^{II}Cl(pdma)_2(4,4'\text{-bpy})]PF_6$,[18] and *trans*-$[Ru^{II}Cl(pdma)_2(bpe)]PF_6$[18] [bpe = *E*-1,2-bis-(4-pyridyl)ethylene] were synthesized by using previously published methods. All other reagents were obtained commercially and used as supplied. The aqueous NH_4PF_6 was ca. 0.6 M. Products were dried overnight in a vacuum desiccator ($CaSO_4$) prior to characterization.

General Physical Measurements. ^1H NMR spectra were recorded on a Varian XL-300 or a Varian Unity 400 spectrometer, and all chemical shifts are quoted with respect to TMS. The midpoints are quoted for multiplet signals. Ring proton numbering and assignments for *fac*-$\{Re^I(biq)(CO)_3\}^+$ units are in accordance with those of Moya et al.,[19] and these were confirmed via COSY studies with selected compounds, including **18** and **19**. Ring proton numbering for 2,2′-bpy derivatives is in accordance with the literature, and assignments were made on the basis of splitting patterns and coupling constants.[20] Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester, and UV−visible spectra were obtained by using a Hewlett-Packard 8452A diode array spectrophotometer. Infrared spectroscopy was performed on KBr disks by using a Perkin-Elmer Spectrum RX1 FT-IR spectrometer. Mass spectra were recorded by using +electrospray on a Micromass Platform II spectrometer, +FAB on a Kratos Concept spectrometer with a 6−8 keV Xe atom beam and 3-nitrobenzyl alcohol as matrix, or +MALDI on a Micromass Tofspec2 by using an acetone solution with an ALPHA matrix.

Cyclic voltammetric measurements were performed on a BAS CV50W voltammetric analyzer. A single-compartment cell was used with a silver/silver chloride reference electrode separated by a salt bridge from a Pt disk working electrode and Pt wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH_2), and $[NBu^n{}_4]PF_6$, purchased from Aldrich and used as supplied, was used as the supporting electrolyte. Solutions containing ca. 10^{-3} M

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analyte (0.1 M electrolyte) were deaerated by purging with N_2. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 200 mV s^{-1}.

Synthesis of 4-Hydroxymethyl-4′-methyl-2,2′-bipyridyl. This compound was prepared according to the method of Berg et al.,[21] except that the intermediate 4-methyl-2,2′-bipyridyl-4′-carbaldehyde was dissolved in ethyl acetate and treated with aqueous Na_2CO_3 as described by Meyer and co-workers[22] prior to reduction with $NaBH_4$. ^{1}H NMR data are consistent with those reported previously.[23]

Synthesis of *trans*-[Ru^{II}Cl(pdma)(4-HOCH$_2$-4′-Me-2,2′-bpy)(NO)](PF$_6$)$_2$ (1). 4-Hydroxymethyl-4′-methyl-2,2′-bipyridyl (700 mg, 3.50 mmol) and *fac*-Ru^{II}Cl$_3$(pdma)(NO) (182 mg, 0.348 mmol) were heated in Ar-degassed methanol (45 mL) under Ar at reflux for 3 h. The mixture changed from an orange suspension to a brown solution as the reaction progressed. The volume was reduced to ca. 3 mL in vacuo, and diethyl ether (100 mL) was added. A brown solid was removed by filtration and washed thoroughly with diethyl ether to remove excess 4-hydroxymethyl-4′-methyl-2,2′-bipyridyl. The solid was dissolved in a minimum volume of water and the resulting solution filtered. Addition of aqueous NH_4PF_6 to the filtrate afforded a beige solid, which was filtered off, washed with water, and dried. Purification was effected by reprecipitation from acetonitrile/diethyl ether to afford the product as a pale beige solid: 218 mg, 66%; δ_H (300 MHz, CD_3CN) 8.80 (1 H, d, $J = 5.7$ Hz, bpyH^6), 8.73 (1 H, d, $J = 5.9$ Hz, bpyH$^{6'}$), 8.65 (1 H, s, bpyH^3), 8.59 (1 H, s, bpyH$^{3'}$), 8.13 (2 H, m, C_6H_4), 7.91 (3 H, m, C_6H_4 and bpyH^5), 7.79 (1 H, d, $J = 6.0$ Hz, bpyH$^{5'}$), 4.96 (2 H, d, $J = 4.2$ Hz, CH_2), 3.98 (1 H, br t, OH), 2.70 (3 H, s, Me), 2.33 (6 H, s, 2AsMe), 2.24 (6 H, s, 2AsMe); $\nu(N{\equiv}O)$ 1874s cm^{-1}. Anal. Calcd (%) for $C_{22}H_{28}N_3As_2ClF_{12}O_2P_2Ru$: C, 28.03; H, 2.99; N, 4.46. Found: C, 28.31; H, 2.89; N, 4.45. ES-MS: $m/z = 797$ ([M − PF$_6$]$^+$), 652 ([M − 2PF$_6$]$^+$), 327 ([M − 2PF$_6$]$^{2+}$).

Synthesis of *trans*-[Ru^{II}Cl(pdma)(4-BrCH$_2$-4′-Me-2,2′-bpy)(NO)](PF$_6$)$_2$ (2). Thionyl bromide (1 mL) was added to **1** (90 mg, 0.095 mmol), and the resulting red solution was stirred at room temperature for 24 h. Aqueous NH_4PF_6 was added dropwise to afford a suspension of cream-colored solid in a clear solution. The solid was filtered off, washed with water, and dried. The crude solid was dissolved in a minimum volume of acetonitrile and filtered to remove an insoluble yellow impurity. Addition of diethyl ether to the filtrate afforded a cream-colored solid, which was filtered off, washed with diethyl ether, and dried: 74 mg, 77%; δ_H (300 MHz, CD_3CN) 8.83 (1 H, d, $J = 5.9$ Hz, bpyH^6), 8.73 (2 H, m, bpyH$^{6'}$ and bpyH^3), 8.58 (1 H, s, bpyH$^{3'}$), 8.13 (2 H, m, C_6H_4), 7.98 (1 H, dd, $J = 5.9$, 1.5 Hz, bpyH^5), 7.92 (2 H, m, C_6H_4), 7.81 (1 H, d, $J = 5.6$ Hz, bpyH$^{5'}$), 4.75 (2 H, s, CH_2), 2.71 (3 H, s, Me), 2.33 (6 H, s, 2AsMe), 2.24 (6 H, s, 2AsMe); $\nu(N{\equiv}O)$ 1875s cm^{-1}. Anal. Calcd (%) for $C_{22}H_{27}N_3As_2BrClF_{12}OP_2Ru$: C, 26.28; H, 2.71; N, 4.18. Found: C, 26.00; H, 2.58; N, 4.17. ES-MS: $m/z = 861$ ([M − PF$_6$]$^+$), 716 ([M − 2PF$_6$]$^+$), 358 ([M − 2PF$_6$]$^{2+}$).

Synthesis of *trans*-[Ru^{II}Cl(pdma)(4-HCO$_2$CH$_2$-4′-Me-2,2′-bpy)(NO)](PF$_6$)$_2$ (3). A solution of **2** (150 mg, 0.149 mmol) and $AgCF_3SO_3$ (150 mg, 0.584 mmol) in dry, Ar-degassed DMF (3 mL) was stirred at room temperature for 24 h. The reaction was protected from light with kitchen foil. The reaction mixture was filtered, and aqueous NH_4PF_6 was added dropwise to the filtrate to afford a pale yellow precipitate. The solid was filtered off, washed with water, and dried. Purification was effected by reprecipitation from acetonitrile/diethyl ether to afford a pale cream-colored solid: 108 mg, 75%; δ_H (300 MHz, CD_3CN) 8.85 (1 H, d, $J = 6.0$ Hz, bpyH^6), 8.73 (1 H, d, $J = 5.7$ Hz, bpyH$^{6'}$), 8.63 (1 H, s, bpyH^3), 8.61 (1 H, s, bpyH$^{3'}$), 8.34 (1 H, s, CH), 8.13 (2 H, m, C_6H_4), 7.91 (3 H, m, C_6H_4 and bpyH^5), 7.80 (1 H, d, $J = 5.9$ Hz, bpyH$^{5'}$), 5.54 (2 H, s, CH_2), 2.71 (3 H, s, Me), 2.33 (6 H, s, 2AsMe), 2.24 (6 H, s, 2AsMe); $\nu(N{\equiv}O)$ 1877s; $\nu(C{=}O)$ 1729s; $\nu(C{-}O)$ 1164s cm^{-1}. Anal. Calcd (%) for $C_{23}H_{28}N_3As_2ClF_{12}O_3P_2Ru$: C, 28.46; H, 2.91; N, 4.33. Found: C, 28.09; H, 2.86; N, 4.34. ES-MS: $m/z = 681$ ([M − 2PF$_6$]$^+$), 651 ([M − 2PF$_6$ − NO]$^+$), 623 ([M − 2PF$_6$ − NO − COH]$^+$).

Synthesis of *fac*-Re^{I}Cl(biq)(CO)$_3$ (4). This known compound was prepared by an adaptation of the method of Wrighton and Morse by using toluene in place of benzene.[24] In a typical preparation, a mixture of Re^I(CO)$_5$Cl (200 mg, 0.55 mmol) and 2,2′-biquinolinyl (284 mg, 1.11 mmol) in Ar-degassed toluene (25 mL) was stirred under Ar at 60 °C for 6 h. A suspension of orange solid in a yellow solution formed. The reaction mixture was cooled to room temperature, and the orange solid was filtered off, washed with toluene followed by pentane, and dried: 195 mg, 63%; δ_H (300 MHz, $CDCl_3$) 9.04 (2 H, d, $J = 8.8$ Hz, H$^{4,4'}$), 8.60 (2 H, d, $J = 8.8$ Hz, H$^{8,8'}$), 8.43 (2 H, d, $J = 8.8$ Hz, H$^{3,3'}$), 8.04 (4 H, m, H$^{5,5'}$ and H$^{7,7'}$), 7.82 (2 H, m, H$^{6,6'}$); $\nu(C{\equiv}O)$ 2014s, 1900s, 1877s cm^{-1}. Anal. Calcd (%) for $C_{21}H_{12}N_2ClO_3Re$: C, 44.88; H, 2.15; N, 4.98. Found: C, 44.03; H, 1.80; N, 4.76. ES-MS: $m/z = 585$ ([M + Na]$^+$).

Synthesis of *fac*-[Re^I(biq)(CO)$_3$(MeCN)]CF$_3$SO$_3$ (5). This known compound[25] was synthesized according to the method used by Guarr and co-workers to prepare *fac*-[Re^I(2,2′-bpy)(CO)$_3$(MeCN)]CF$_3$SO$_3$ by using complex **4** (64 mg, 0.114 mmol) in place of *fac*-Re^{I}Cl(2,2′-bpy)(CO)$_3$.[14] After rotary evaporation, the red solid residue was dissolved in a minimum volume of chloroform and filtered, and the filtrate was carefully layered with diethyl ether. After refrigeration for 2 days, dark orange crystals (suitable for X-ray diffraction studies) were filtered off, washed with diethyl ether, and dried: 83 mg, 87%; δ_H (300 MHz, $CDCl_3$) 9.11 (2 H, d, $J = 8.8$ Hz, H$^{4,4'}$), 8.84 (2 H, d, $J = 8.8$ Hz, H$^{8,8'}$), 8.77 (2 H, d, $J = 8.8$ Hz, H$^{3,3'}$), 8.08 (4 H, m, H$^{5,5'}$ and H$^{7,7'}$), 7.86 (2 H, m, H$^{6,6'}$), 2.16 (3 H, s, MeCN); $\nu(C{\equiv}O)$ 2034s, 1936s br cm^{-1}. Anal. Calcd (%) for $C_{24}H_{15}N_3F_3O_6ReS\cdot CHCl_3$: C, 35.92; H, 1.93; N, 5.03. Found: C, 36.60; H, 1.86; N, 5.02. ES-MS: $m/z = 568$ ([M − CF$_3$SO$_3$]$^+$).

Synthesis of *fac*-[Re^I(biq)(CO)$_3$(py)]CF$_3$SO$_3$ (6). A solution of **5**·CHCl$_3$ (130 mg, 0.155 mmol) and pyridine (ca. 400 mg, 5 mmol) was heated under reflux in Ar-degassed methanol (30 mL) under Ar for 3 h. The volume was reduced in vacuo to ca. 5 mL, and diethyl ether (200 mL) was added slowly to the red solution to afford an orange microcrystalline precipitate. The solid was filtered off, washed with diethyl ether, and dried: 79 mg, 67%; δ_H (300 MHz, CD_3CN) 9.10 (2 H, d, $J = 8.8$ Hz, biqH$^{4,4'}$), 9.03 (2 H, d, $J = 8.8$ Hz, biqH$^{8,8'}$), 8.82 (2 H, d, $J = 8.8$ Hz, biqH$^{3,3'}$), 8.36 (4 H, m, biqH$^{5,5'}$ and biqH$^{7,7'}$), 8.07 (2 H, m, biqH$^{6,6'}$), 7.94 (1 H, t, $J = 7.7$ Hz, pyH^4), 7.65 (2 H, d, $J = 5.0$ Hz, pyH^2), 7.26 (2 H, m, pyH^3); $\nu(C{\equiv}O)$ 2028s, 1922s br cm^{-1}. Anal. Calcd (%) for $C_{27}H_{17}N_3F_3O_6ReS$: C, 42.97; H, 2.27; N, 5.57. Found: C, 42.53; H, 2.04; N, 5.50. ES-MS: $m/z = 606$ ([M − CF$_3$SO$_3$]$^+$).

Synthesis of *fac*-[Re^I(biq)(CO)$_3$(4-HOCH$_2$C$_5$H$_4$N)]CF$_3$SO$_3$ (7). A solution of **5**·CHCl$_3$ (188 mg, 0.225 mmol) and 4-(hydroxymethyl)pyridine (288 mg, 2.64 mmol) was heated under reflux in Ar-degassed methanol (30 mL) under Ar for 3 h. The volume was reduced in vacuo to ca. 15 mL, and diethyl ether (200 mL) was added slowly to the red solution to afford an orange microcrystalline precipitate. The solid was filtered off, washed with diethyl ether, and dried: 154 mg, 85%; δ_H (300 MHz, CD_3COCD_3) 9.12 (2 H, d, $J = 8.6$ Hz, biqH$^{4,4'}$), 9.06 (2 H, d, $J = 8.8$ Hz, biqH$^{8,8'}$), 8.85 (2 H, d, $J = 8.8$ Hz, biqH$^{3,3'}$), 8.43 (2 H, d, $J = 8.1$ Hz, biqH$^{5,5'}$),

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8.37 (2 H, m, biqH$^{7,7'}$), 8.10 (2 H, m, biqH$^{6,6'}$), 7.57 (2 H, d, J = 6.6 Hz, C_5H_4N), 7.24 (2 H, d, J = 6.6 Hz, C_5H_4N), 4.76 (1 H, t, J = 5.1 Hz, OH), 4.62 (2 H, d, J = 5.1 Hz, CH_2); ν(C≡O) 2029s, 1918s br cm^{-1}. Anal. Calcd (%) for $C_{28}H_{19}N_3F_3O_7ReS$: C, 42.86; H, 2.44; N, 5.35. Found: C, 42.54; H, 2.30; N, 5.27.

Synthesis of *fac*-[Re^{I}(biq)(CO)$_3$(4-BrCH$_2$C$_5$H$_4$N)]PF$_6$ (8). Thionyl bromide (2 mL) was added to **7** (143 mg, 0.182 mmol), and the red solution was stirred at room temperature for 24 h. Aqueous NH_4PF_6 was added dropwise with stirring until a suspension of orange solid in a clear solution had formed. The solid was filtered off, washed with water, and dried. The crude product was dissolved in a minimum volume of acetonitrile and filtered to remove insoluble impurities. Aqueous NH_4PF_6 was added to the filtrate, and an orange solid precipitate was filtered off, washed with water, and dried: 105 mg, 68%; δ_H (300 MHz, CD_3COCD_3) 9.14 (2 H, d, J = 8.8 Hz, biqH$^{4,4'}$), 9.06 (2 H, d, J = 8.8 Hz, biqH$^{8,8'}$), 8.86 (2 H, d, J = 8.8 Hz, biqH$^{3,3'}$), 8.44 (2 H, d, J = 8.2 Hz, biqH$^{5,5'}$), 8.38 (2 H, m, biqH$^{7,7'}$), 8.12 (2 H, m, biqH$^{6,6'}$), 7.73 (2 H, d, J = 6.7 Hz, C_5H_4N), 7.37 (2 H, d, J = 6.7 Hz, C_5H_4N), 4.55 (2 H, s, CH_2); ν(C≡O) 2029s, 1926s, 1914s cm^{-1}. Anal. Calcd (%) for $C_{27}H_{18}N_3BrF_6O_3PRe$: C, 38.45; H, 2.15; N, 4.98. Found: C, 38.76; H, 2.02; N, 4.88. ES-MS: m/z = 698 ([M − PF$_6$]$^+$). Single crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether vapor into a concentrated dichloromethane solution at room temperature.

Synthesis of *fac*-[Re^{I}(biq)(CO)$_3$(4-HCO$_2$CH$_2$C$_5$H$_4$N)]PF$_6$ (9). This compound was prepared in a manner similar to **3**, by using **8** (50 mg, 0.059 mmol) and $AgCF_3SO_3$ (60 mg, 0.234 mmol). Purification was effected by reprecipitation from acetone/diethyl ether to afford a red, microcrystalline solid: 41 mg, 86%; δ_H (300 MHz, CD_3COCD_3) 9.08 (2 H, d, J = 8.6 Hz, biqH$^{4,4'}$), 9.02 (2 H, d, J = 8.9 Hz, biqH$^{8,8'}$), 8.79 (2 H, d, J = 8.8 Hz, biqH$^{3,3'}$), 8.39 (2 H, d, J = 8.1 Hz, biqH$^{5,5'}$), 8.33 (2 H, m, biqH$^{7,7'}$), 8.19 (1 H, s, CH), 8.06 (2 H, m, biqH$^{6,6'}$), 7.66 (2 H, d, J = 6.7 Hz, C_5H_4N), 7.25 (2 H, d, J = 6.7 Hz, C_5H_4N), 5.18 (2 H, s, CH_2); ν(C≡O) 2036s, 1939s, 1914s; ν(C=O) 1723s; ν(C−O) 1172s cm^{-1}. Anal. Calcd (%) for $C_{28}H_{19}N_3F_6O_5PRe\cdot Me_2CO$: C, 42.96; H, 2.91; N, 4.85. Found: C, 42.62; H, 2.86; N, 4.81. MALDI-MS: m/z = 664 ([M − PF$_6$]$^+$). Single crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether vapor into a concentrated acetone solution at room temperature.

Synthesis of *trans,trans*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(4-CH$_2$-4′-Me-2,2′-bpy)}Ru^{II}Cl(pdma)(NO)](PF$_6$)$_4$ (10). A solution of *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$ (225 mg, 0.223 mmol), **2** (112 mg, 0.111 mmol), and $AgCF_3SO_3$ (47 mg, 0.183 mmol) in dry, Ar-degassed DMF (2 mL) was stirred at room temperature for 13 days. The reaction mixture was protected from light with kitchen foil. The crude mixture was filtered through Celite, aqueous NH_4PF_6 was added to the filtrate, and a brown solid was filtered off, washed with water, and dried. The solid was dissolved in a minimum volume of acetone, and a saturated solution of LiCl in acetone was added dropwise until a purple solid precipitated. Filtration gave a purple solid and an orange filtrate (note: the filtrate contains the excess *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$, which may be recovered by addition of aqueous NH_4PF_6 and extraction into dichloromethane). The purple solid was dissolved in a minimum volume of water, aqueous NH_4PF_6 was added, and the precipitate was filtered off. The crude product was loaded onto a silica gel column and eluted with acetone/water/KNO$_3$(aq, sat) (16:2:1 v/v). The column was protected from light with kitchen foil. The major purple band was collected, aqueous NH_4PF_6 was added, and the acetone was removed in vacuo. The resultant suspension was extracted into acetone/CH_2Cl_2 (1:9 v/v) and the organic layer evaporated to a few millliliters in vacuo. The addition of diethyl ether afforded the pure product as a deep purple solid, which was filtered off, washed with diethyl ether, and dried: 77 mg, 33%; δ_H (400 MHz, CD_3COCD_3) 9.29 (2 H, d, J = 7.2 Hz, C_5H_4N), 9.25 (1 H, d, J = 6.0 Hz, 2,2′-bpyH$^{6'}$), 9.21 (1 H, d, J = 6.0 Hz, 2,2′-bpyH^{6}), 9.11 (1 H, s, 2,2′-bpyH^{3}), 8.75 (1 H, s, 2,2′-bpyH$^{3'}$), 8.49 (2 H, d, J = 6.8 Hz, C_5H_4N), 8.40 (2 H, m, C_6H_4), 8.31 (4 H, m, C_6H_4), 7.95 (6 H, m, C_6H_4, C_5H_4N, and 2,2′-bpyH$^{5,5'}$), 7.83 (4 H, m, C_6H_4), 7.63 (2 H, d, J = 7.2 Hz, C_5H_4N), 6.44 (2 H, s, CH_2), 2.68 (3 H, s, Me), 2.57 (3 H, s, AsMe), 2.48 (3 H, s, AsMe), 2.43 (3 H, s, AsMe), 2.34 (3 H, s, AsMe), 1.90 (12 H, s, 4AsMe), 1.80 (12 H, s, 4AsMe); ν(N≡O) 1893s cm^{-1}. Anal. Calcd (%) for $C_{52}H_{67}N_5As_6Cl_2F_{24}OP_4Ru_2$: C, 30.02; H, 3.25; N, 3.37. Found: C, 29.93; H, 3.05; N, 3.33. FAB-MS: m/z = 1935 ([M − PF$_6$]$^+$), 1791 ([M − 2PF$_6$]$^+$), 1645 ([M − 3PF$_6$]$^+$).

Synthesis of *trans,trans*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(4-CH$_2$-4′-Me-2,2′-bpy)}Ru^{II}Cl(pdma)(NO)](PF$_6$)$_4$ (11). This compound was prepared and purified in a manner similar to **10**, by using *trans*-[Ru^{II}Cl(pdma)$_2$(bpe)]PF$_6$ (178 mg, 0.172 mmol) in place of *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$, **2** (86 mg, 0.086 mmol), and $AgCF_3SO_3$ (38 mg, 0.148 mmol), with a reaction time of 10 days. A deep purple solid was obtained: 69 mg, 38%; δ_H (400 MHz, CD_3COCD_3) 9.31 (1 H, d, J = 6.0 Hz, 2,2′-bpyH$^{6'}$), 9.22 (1 H, d, J = 6.0 Hz, 2,2′-bpyH^{6}), 9.13 (2 H, d, J = 7.2 Hz, C_5H_4N), 9.11 (1 H, d, J = 1.6 Hz, 2,2′-bpyH$^{3'}$), 8.75 (1 H, s, 2,2′-bpyH^{3}), 8.40 (2 H, m, C_6H_4), 8.30 (6 H, m, C_6H_4 and C_5H_4N), 8.00 (1 H, dd, J = 6.0, 2.0 Hz, 2,2′-bpyH^{5}), 7.95 (3 H, m, C_6H_4 and 2,2′-bpyH$^{5'}$), 7.82 (5 H, m, C_6H_4 and CH), 7.74 (2 H, d, J = 6.8 Hz, C_5H_4N), 7.66 (1 H, d, J = 16.4 Hz, CH), 7.32 (2 H, d, J = 7.2 Hz, C_5H_4N), 6.37 (2 H, s, CH_2), 2.69 (3 H, s, Me), 2.57 (3 H, s, AsMe), 2.50 (3 H, s, AsMe), 2.44 (3 H, s, AsMe), 2.37 (3 H, s, AsMe), 1.89 (12 H, s, 4AsMe), 1.79 (12 H, s, 4AsMe); ν(N≡O) 1895s cm^{-1}. Anal. Calcd (%) for $C_{54}H_{69}N_5As_6Cl_2F_{24}OP_4Ru_2$: C, 30.79; H, 3.30; N, 3.32. Found: C, 30.57; H, 3.22; N, 3.22.

Synthesis of *trans,fac*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(4-CH$_2$C$_5$H$_4$N)}Re^{I}(biq)(CO)$_3$](PF$_6$)$_3$ (12). This compound was prepared and purified in a manner similar to **10**, by using *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$ (119 mg, 0.118 mmol), **8** (50 mg, 0.059 mmol), and $AgCF_3SO_3$ (25 mg, 0.097 mmol), with a reaction time of 7 days. A deep purple solid was obtained: 34 mg, 30%; δ_H (400 MHz, CD_3COCD_3) 9.00 (2 H, d, J = 8.8 Hz, biqH$^{4,4'}$), 8.98 (2 H, d, J = 7.2 Hz, $C_5H_4N_{4,4'-bpy}$), 8.95 (2 H, dd, J = 8.8, 0.8 Hz, biqH$^{8,8'}$), 8.68 (2 H, d, J = 8.8 Hz, biqH$^{3,3'}$), 8.39 (2 H, d, J = 6.8 Hz, $C_5H_4N_{4,4'-bpy}$), 8.34 (2 H, d, J = 8.1 Hz, biqH$^{5,5'}$), 8.31 (4 H, m, C_6H_4), 8.28 (2 H, m, biqH$^{7,7'}$), 8.02 (2 H, m, biqH$^{6,6'}$), 7.93 (2 H, d, J = 7.2 Hz, $C_5H_4N_{4,4'-bpy}$), 7.84 (4 H, m, C_6H_4), 7.61 (2 H, d, J = 6.8 Hz, C_5H_4N), 7.57 (2 H, d, J = 6.8 Hz, $C_5H_4N_{4,4'-bpy}$), 7.15 (2 H, d, J = 6.8 Hz, C_5H_4N), 1.90 (12 H, s, 4AsMe), 1.79 (12 H, s, 4AsMe); ν(C≡O) 2033s, 1920s br cm^{-1}. Anal. Calcd (%) for $C_{57}H_{58}N_5As_4ClF_{18}O_3P_3ReRu$: C, 35.69; H, 3.05; N, 3.65. Found: C, 35.27; H, 2.48; N, 3.47. FAB-MS: m/z = 1943 ([M + Na]$^+$), 1798 ([M − PF$_6$ + Na]$^+$), 1775 ([M − PF$_6$]$^+$), 1629 ([M − 2PF$_6$]$^+$), 1484 ([M − 3PF$_6$]$^+$).

Synthesis of *trans,fac*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(4-CH$_2$C$_5$H$_4$N)}-Re^{I}(biq)(CO)$_3$](PF$_6$)$_3$ (13). This compound was prepared and purified in a manner similar to **12**, by using *trans*-[Ru^{II}Cl(pdma)$_2$(bpe)]PF$_6$ (122 mg, 0.118 mmol) in place of *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$. A deep purple solid was obtained: 33 mg, 29%; δ_H (400 MHz, CD_3COCD_3) 9.01 (2 H, d, J = 8.8 Hz, biqH$^{4,4'}$), 8.97 (2 H, dd, J = 8.8, 0.8 Hz, biqH$^{8,8'}$), 8.89 (2 H, d, J = 6.8 Hz, $C_5H_4N_{bpe}$), 8.74 (2 H, d, J = 8.8 Hz, biqH$^{3,3'}$), 8.35 (2 H, d, J = 8.1 Hz, biqH$^{5,5'}$), 8.30 (6 H, m, C_6H_4 and biqH$^{7,7'}$), 8.22 (2 H, d, J = 6.8 Hz, $C_5H_4N_{bpe}$), 8.02 (2 H, m, biqH$^{6,6'}$), 7.83 (4 H, m, C_6H_4), 7.78 (2 H, d, J = 16.0 Hz, CH), 7.73 (2 H, d, J = 6.8 Hz, $C_5H_4N_{bpe}$), 7.63 (2 H, d, J = 6.8 Hz, C_5H_4N), 7.58 (2 H, d, J = 16.0 Hz, CH), 7.29 (2 H, d, J = 6.8 Hz, $C_5H_4N_{bpe}$), 7.20 (2 H, d, J = 6.8 Hz, C_5H_4N), 1.90 (12 H, s, 4AsMe), 1.70 (12 H, s, 4AsMe); ν(C≡O) 2031s, 1920s br cm^{-1}. Anal. Calcd (%) for $C_{59}H_{60}N_5As_4ClF_{18}O_3P_3ReRu$: C, 36.44; H, 3.11; N, 3.60. Found: C, 36.03; H, 3.15; N, 3.82.

Synthesis of *trans*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(C$_2$H$_4$NH$_3$)}](PF$_6$)$_3$ (14). 2-Bromoethylamine hydrobromide (152 mg, 0.742 mmol) was heated to reflux in acetonitrile (10 mL). To this solution was added a solution of *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$ (150 mg, 0.149 mmol) in acetonitrile (10 mL), followed by AgBF$_4$ (289 mg, 1.49 mmol). The reaction mixture was protected from light with kitchen foil and stirred under reflux for 4 h before cooling to room temperature. The mixture was filtered to remove AgBr, the filtrate reduced in volume to ca. 1 mL, and aqueous NH$_4$PF$_6$ added to produce a red precipitate, which was filtered off and dried in vacuo. Purification was effected by sequential reprecipitations from acetone/LiCl, water/aqueous NH$_4$PF$_6$, and finally acetone/diethyl ether to afford a red solid: 90 mg, 45%; δ_H (400 MHz, CD$_3$COCD$_3$) 9.24 (2 H, d, *J* = 7.2 Hz, C$_5$H$_4$N), 8.45 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 8.31 (4 H, m, C$_6$H$_4$), 7.94 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 7.84 (4 H, m, C$_6$H$_4$), 7.63 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 5.31 (2 H, t, *J* = 5.8 Hz, CH$_2$), 4.65 (2 H, br s, CH$_2$), 1.90 (12 H, s, 4AsMe), 1.79 (12 H, s, 4AsMe). Anal. Calcd (%) for C$_{32}$H$_{46}$As$_4$ClF$_{12}$N$_3$P$_2$Ru·HPF$_6$: C, 28.58; H, 3.52; N, 3.12. Found: C, 28.31; H, 3.33; N, 3.03. MALDI-MS: *m*/*z* = 907 ([M − 3HPF$_6$]$^+$).

Synthesis of *trans*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(C$_2$H$_4$NH$_3$)}](PF$_6$)$_3$ (15). This compound was prepared and purified in a manner similar to **14**, by using *trans*-[Ru^{II}Cl(pdma)$_2$(bpe)]PF$_6$ (150 mg, 0.145 mmol) in place of *trans*-[Ru^{II}Cl(pdma)$_2$(4,4′-bpy)]PF$_6$, 2-bromoethylamine hydrobromide (148 mg, 0.724 mmol), and AgBF$_4$ (282 mg, 1.45 mmol). The product was obtained as a dark red solid: 93 mg, 47%; δ_H (400 MHz, CD$_3$COCD$_3$) 9.03 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 8.30 (4 H, m, C$_6$H$_4$), 8.26 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 7.83 (4 H, m, C$_6$H$_4$), 7.77 (1 H, d, *J* = 16.4 Hz, CH), 7.73 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 7.61 (1 H, d, *J* = 16.4 Hz, CH), 7.30 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 5.16 (2 H, t, *J* = 5.8 Hz, CH$_2$), 4.53 (2 H, br s, CH$_2$), 1.89 (12 H, s, 4AsMe), 1.78 (12 H, s, 4AsMe). Anal. Calcd (%) for C$_{34}$H$_{48}$As$_4$ClF$_{12}$N$_3$P$_2$Ru·HPF$_6$: C, 29.79; H, 3.60; N, 3.07. Found: C, 29.03; H, 3.64; N, 3.16. ES-MS: *m*/*z* = 1079 ([M − 2HPF$_6$]$^+$), 933 ([M − 3HPF$_6$]$^+$).

Synthesis of *fac*-[Re^{I}(biq)(CO)$_3$(ISNE)]CF$_3$SO$_3$ (16). A solution of **5**·CHCl$_3$ (100 mg, 0.120 mmol) and ethyl isonicotinate (585 mg, 3.87 mmol) was heated under reflux in methanol (25 mL) for 3 h. The volume was reduced in vacuo to ca. 1 mL, and diethyl ether was added slowly to afford an orange, microcrystalline precipitate, which was filtered off, washed with diethyl ether, and dried: 91 mg, 92%; δ_H (400 MHz, CDCl$_3$) 8.95 (2 H, d, *J* = 8.8 Hz, biqH$^{4,4'}$), 8.88 (4 H, m, biqH$^{8,8'}$ and biqH$^{3,3'}$), 8.16 (4 H, m, biqH$^{5,5'}$ and biqH$^{7,7'}$), 7.94 (2 H, m, biqH$^{6,6'}$), 7.59 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 7.37 (2 H, d, *J* = 6.4 Hz, C$_5$H$_4$N), 4.33 (2 H, q, *J* = 7.2 Hz, CH$_2$), 1.30 (2 H, t, *J* = 7.2 Hz, Me); ν(C≡O) 2036s, 1937s, 1915s; ν(C═O) 1728s; ν(C−O) 1261s, 1031s cm^{-1}. Anal. Calcd (%) for C$_{30}$H$_{21}$F$_3$N$_3$O$_8$ReS: C, 43.58; H, 2.56; N, 5.08. Found: C, 43.29; H, 2.54; N, 4.86. ES-MS: *m*/*z* = 678 ([M − CF$_3$SO$_3$]$^+$). Crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether vapor into a concentrated chloroform solution at room temperature.

Synthesis of *fac*-[Re^{I}(biq)(CO)$_3$(ISNA)]PF$_6$ (17). To a solution of **16** (95 mg, 0.115 mmol) in methanol (5 mL) was added 2% aqueous NaOH (1 mL), and the reaction stirred at room temperature for 7 h. The reaction was acidified by the addition of sulfuric acid (98%, 5 drops) and the product precipitated by the addition of aqueous NH$_4$PF$_6$. After standing for 30 min in a refrigerator, the yellow solid was filtered off, washed with water, and dried: 91 mg, 100%; δ_H (400 MHz, CD$_3$CN) 8.95 (2 H, d, *J* = 8.8 Hz, biqH$^{4,4'}$), 8.83 (2 H, d, *J* = 8.8 Hz, biqH$^{8,8'}$), 8.37 (2 H, d, *J* = 8.8 Hz, biqH$^{3,3'}$), 8.23 (4 H, m, biqH$^{5,5'}$ and biqH$^{7,7'}$), 7.99 (2 H, m, biqH$^{6,6'}$), 7.49 (2 H, d, *J* = 6.0 Hz, C$_5$H$_4$N), 7.41 (2 H, d, *J* = 6.0 Hz, C$_5$H$_4$N); ν(C≡O) 2031s, 1924s, 1906s; ν(C═O) 1719s cm^{-1}. Anal. Calcd (%) for C$_{27}$H$_{17}$F$_6$N$_3$O$_5$PRe: C, 40.81; H, 2.16; N, 5.29. Found: C, 40.78; H, 2.40; N, 5.12. ES-MS: *m*/*z* = 650 ([M − PF$_6$]$^+$), 527 ([M − PF$_6$ − ISNA]$^+$). Crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether vapor into a concentrated acetonitrile solution at room temperature.

Synthesis of *trans,fac*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(C$_2$H$_4$NHCO-4-C$_5$H$_4$N)}Re^{I}(biq)(CO)$_3$](PF$_6$)$_3$ (18). To a solution of **14** (95 mg, 0.079 mmol) in dry DMF (5 mL) was added **17** (63 mg, 0.079 mmol), 1-hydroxybenzotriazole (HOBT, 16 mg, 0.118 mmol), and 1,3-diisopropylcarbodiimide (DIC, 0.04 mL, 0.255 mmol). The reaction mixture was protected from light with kitchen foil and stirred at room temperature for 7 h. Addition of aqueous NH$_4$PF$_6$ gave a red precipitate, which was filtered off, washed with water, and dried in vacuo. Purification was effected via column chromatography exactly as for **10**, except that the acetone was not removed in vacuo before extraction into acetone/CH$_2$Cl$_2$ (1:9 v/v), and a final reprecipitation from acetone/diethyl ether afforded a deep red solid: 61 mg, 44%; δ_H (400 MHz, CD$_3$COCD$_3$) 9.03 (4 H, m, biqH$^{4,4'}$ and C$_5$H$_4$N$_{4,4'\text{-bpy}}$), 8.96 (2 H, d, *J* = 8.8 Hz, biqH$^{8,8'}$), 8.22 (2 H, d, *J* = 8.8 Hz, biqH$^{3,3'}$), 8.36 (2 H, d, *J* = 8.4 Hz, biqH$^{5,5'}$), 8.34−8.28 (8 H, m, biqH$^{7,7'}$, C$_6$H$_4$ and C$_5$H$_4$N$_{4,4'\text{-bpy}}$), 8.15 (1 H, t, *J* = 5.8 Hz, NH), 8.05 (2 H, m, biqH$^{6,6'}$), 7.90 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N$_{4,4'\text{-bpy}}$), 7.85 (4 H, m, C$_6$H$_4$), 7.76 (2 H, d, *J* = 6.4 Hz, C$_5$H$_4$N), 7.55 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N$_{4,4'-\text{bpy}}$), 7.41 (2 H, d, *J* = 6.4 Hz, C$_5$H$_4$N), 4.87 (2 H, t, *J* = 5.2 Hz, CH$_2$), 3.96 (2 H, m, CH$_2$), 1.91 (12 H, s, 4AsMe), 1.79 (12 H, s, 4AsMe); ν(C≡O) 2033s, 1923br; ν(C═O) 1708s cm^{-1}. Anal. Calcd (%) for C$_{59}$H$_{61}$N$_6$As$_4$ClF$_{18}$O$_4$P$_3$ReRu: C, 35.87; H, 3.11; N, 4.25. Found: C, 35.56; H, 2.94; N, 4.16. MALDI-MS: *m*/*z* = 1563 ([M − 3PF$_6$ + Na]$^+$), 1014 [(M − 3PF$_6$ − Re(biq)(CO)$_3$]$^+$).

Synthesis of *trans,fac*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(C$_2$H$_4$NHCO-4-C$_5$H$_4$N)}Re^{I}(biq)(CO)$_3$](PF$_6$)$_3$ (19). This compound was prepared and purified in a manner similar to **18** by using **15** (75 mg, 0.055 mmol), in place of **14**, and **17** (49 mg, 0.062 mmol). A final reprecipitation from acetone/aqueous NH$_4$PF$_6$ gave a dark red solid: 59 mg, 53%; δ_H (400 MHz, CD$_3$COCD$_3$) 9.03 (2 H, d, *J* = 8.8 Hz, biqH$^{4,4'}$), 8.96 (2 H, d, *J* = 9.2 Hz, biqH$^{8,8'}$), 8.89 (2 H, d, *J* = 7.2 Hz, C$_5$H$_4$N$_{\text{bpe}}$), 8.73 (2 H, d, *J* = 8.8 Hz, biqH$^{3,3'}$), 8.36 (2 H, d, *J* = 7.2 Hz, biqH$^{5,5'}$), 8.33−8.27 (6 H, m, C$_6$H$_4$ and biqH$^{7,7'}$), 8.23 (1 H, t, *J* = 5.8 Hz, NH), 8.12 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N$_{\text{bpe}}$), 8.04 (2 H, m, biqH$^{6,6'}$), 7.84 (4 H, m, C$_6$H$_4$), 7.78 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 7.73 (2 H, d, *J* = 7.2 Hz, C$_5$H$_4$N$_{\text{bpe}}$), 7.68 (1 H, d, *J* = 16.4 Hz, CH), 7.53 (1 H, d, *J* = 16.4 Hz, CH), 7.43 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N), 7.28 (2 H, d, *J* = 6.8 Hz, C$_5$H$_4$N$_{\text{bpe}}$), 4.82 (2 H, t, *J* = 5.4 Hz, CH$_2$), 3.97 (2 H, m, CH$_2$), 1.91 (12 H, s, 4AsMe), 1.79 (12 H, s, 4AsMe); ν(C≡O) 2033s, 1922br; ν(C═O) 1708s cm^{-1}. Anal. Calcd (%) for C$_{61}$H$_{63}$N$_6$As$_4$ClF$_{18}$O$_4$P$_3$ReRu·2H$_2$O: C, 35.96; H, 3.31; N, 4.12. Found: C, 35.73; H, 2.98; N, 4.10. MALDI-MS: *m*/*z* = 1564 ([M − 3PF$_6$]$^+$).

X-ray Crystallographic Studies. For all five salts **5**·CHCl$_3$, **8**, **9**·Me$_2$CO, **16**, and *fac*-[Re^{I}(biq)(CO)$_3$(NC$_5$H$_4$CO$_2$)]$_2$·HPF$_6$·3MeCN (**17D**·3MeCN, derived from **17**), data were collected on a Nonius Kappa CCD area-detector diffractometer controlled by the Collect software package.[26] The data were processed by Denzo[27] and corrected for absorption by using the empirical method employed in Sortav[28] from within the MAXUS suite of programs.[29] The structures were solved by direct methods and refined by full-matrix least-squares on all F_o^2 data by using SHELXS-97[30] and SHELXL-97.[31] All non-hydrogen atoms were refined anisotropically with

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Table 1. UV−Visible Absorption and Electrochemical Data for Complexes and Complex Salts in Acetonitrile

compound	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]	assignment	$E_{1/2}$ or E, V vs Ag−AgCl (ΔE_p, mV)[b] oxidations	 reductions
trans-[Ru^{II}Cl(pdma)(2,2′-bpy)(NO)](PF$_6$)$_2$[c]	234 (27 700)	$\pi \rightarrow \pi^*$		0.10 (80)
	298 (8100)	$\pi \rightarrow \pi^*$		−0.52[d]
	322 (7200)	d $\rightarrow \pi^*$		
1 *trans*-[Ru^{II}Cl(pdma)(4-HOCH$_2$-4′-Me-2,2′-bpy)(NO)](PF$_6$)$_2$	298 (11 400)	$\pi \rightarrow \pi^*$		0.16 (230)
	318 (12 900)	d $\rightarrow \pi^*$		−0.67[d]
2 *trans*-[Ru^{II}Cl(pdma)(4-BrCH$_2$-4′-Me-2,2′-bpy)(NO)](PF$_6$)$_2$	288 (27 900)	$\pi \rightarrow \pi^*$		0.16 (170)
	324sh (14 200)	d $\rightarrow \pi^*$		−0.68[d]
3 *trans*-[Ru^{II}Cl(pdma)(4-HCO$_2$CH$_2$-4′-Me-2,2′-bpy)(NO)](PF$_6$)$_2$	236 (36 500)	$\pi \rightarrow \pi^*$		0.11 (85)
	302 (9400)	$\pi \rightarrow \pi^*$		−0.49[d]
	320 (8800)	d $\rightarrow \pi^*$		
trans-[Ru^{II}Cl(pdma)$_2$(MeQ$^+$)](PF$_6$)$_2$[e]	486 (8300)	d $\rightarrow \pi^*$	1.16 (70)	−0.72 (80)
				−1.26 (80)
trans-[Ru^{II}Cl(pdma)$_2$(Mebpe$^+$)](PF$_6$)$_2$[f]	316 (28 500)	d $\rightarrow \pi^*$	1.12 (95)	−0.77[d]
	492 (13 000)			
4 *fac*-Re^{I}Cl(biq)(CO)$_3$	266 (42 400)	$\pi \rightarrow \pi^*$	1.52[g]	−0.86 (70)
	306sh (13 800)	$\pi \rightarrow \pi^*$		
	354 (20 000)	d $\rightarrow \pi^*$		
	372 (30 500)	d $\rightarrow \pi^*$		
	426 (3900)	d $\rightarrow \pi^*$		
5 *fac*-[Re^I(biq)(CO)$_3$(MeCN)]CF$_3$SO$_3$	268 (44 100)	$\pi \rightarrow \pi^*$		−0.69 (55)
	308sh (10 200)	$\pi \rightarrow \pi^*$		−1.19[d]
	360 (19 500)	d $\rightarrow \pi^*$		
	376 (27 100)	d $\rightarrow \pi^*$		
6 *fac*-[Re^I(biq)(CO)$_3$(py)]CF$_3$SO$_3$	270 (43 500)	$\pi \rightarrow \pi^*$		−0.63 (75)
	308sh (13 500)	$\pi \rightarrow \pi^*$		−1.13 (80)
	362 (19 200)	d $\rightarrow \pi^*$		
	378 (26 500)	d $\rightarrow \pi^*$		
7 *fac*-[Re^I(biq)(CO)$_3$(4-HOCH$_2$C$_5$H$_4$N)]CF$_3$SO$_3$	268 (41 800)	$\pi \rightarrow \pi^*$		−0.64 (70)
	310sh (11 300)	$\pi \rightarrow \pi^*$		−1.17 (65)
	360 (18 300)	d $\rightarrow \pi^*$		
	378 (25 900)	d $\rightarrow \pi^*$		
8 *fac*-[Re^I(biq)(CO)$_3$(4-BrCH$_2$C$_5$H$_4$N)]PF$_6$	268 (41 000)	$\pi \rightarrow \pi^*$	0.87[g]	−0.64[d]
	310sh (13 300)	$\pi \rightarrow \pi^*$		−1.21[d]
	362 (17 700)	d $\rightarrow \pi^*$		
	378 (24 700)	d $\rightarrow \pi^*$		
9 *fac*-[Re^I(biq)(CO)$_3$(4-HCO$_2$CH$_2$C$_5$H$_4$N)]PF$_6$	268 (43 700)	$\pi \rightarrow \pi^*$		−0.64 (70)
	308sh (14 000)	$\pi \rightarrow \pi^*$		−1.22[d]
	360 (18 600)	d $\rightarrow \pi^*$		
	378 (25 600)	d $\rightarrow \pi^*$		
10 *trans,trans*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(4-CH$_2$-4′-Me-2,2′-bpy)}Ru^{II}Cl(pdma)(NO)](PF$_6$)$_4$	320sh (11 400)	d $\rightarrow \pi^*$(2,2′-bpy)	1.18 (85)	0.12 (145)
	510 (9600)	d $\rightarrow \pi^*$(4,4′-bpy)		
11 *trans,trans*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(4-CH$_2$-4′-Me-2,2′-bpy)}Ru^{II}Cl(pdma)(NO)](PF$_6$)$_4$	320 (36 300)	$\pi \rightarrow \pi^*$(C=C)	1.11 (75)	0.09 (130)
	518 (12 800)	d $\rightarrow \pi^*$(bpe)		
12 *trans,fac*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(4-CH$_2$C$_5$H$_4$N)}Re^I(biq)(CO)$_3$](PF$_6$)$_3$	268 (55 100)	$\pi \rightarrow \pi^*$	1.13 (75)	
	362 (17 800)	d $\rightarrow \pi^*$(biq)		
	378 (25 300)	d $\rightarrow \pi^*$(biq)		
	506 (9600)	d $\rightarrow \pi^*$(4,4′-bpy)		
13 *trans,fac*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(4-CH$_2$C$_5$H$_4$N)}Re^I(biq)(CO)$_3$](PF$_6$)$_3$	270 (58 800)	$\pi \rightarrow \pi^*$	1.12 (70)	
	310 (47 600)	$\pi \rightarrow \pi^*$(C=C)		
	362 (24 600)	d $\rightarrow \pi^*$(biq)		
	378 (31 300)	d $\rightarrow \pi^*$(biq)		
	506 (15 300)	d $\rightarrow \pi^*$(bpe)		
14 *trans*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(C$_2$H$_4$NH$_3$)}](PF$_6$)$_3$	262 (24 200)	$\pi \rightarrow \pi^*$	1.18 (60)	−0.71 (65)
	488 (7600)	d $\rightarrow \pi^*$		−1.27 (65)
15 *trans*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(C$_2$H$_4$NH$_3$)}](PF$_6$)$_3$	314 (25 200)	$\pi \rightarrow \pi^*$	1.13 (60)	−0.67 (70)
	496 (10 400)	d $\rightarrow \pi^*$		−1.44[d]
16 *fac*-[Re^I(biq)(CO)$_3$(ISNE)]CF$_3$SO$_3$	270 (39 000)	$\pi \rightarrow \pi^*$		−0.65 (70)
	308sh (12 000)	$\pi \rightarrow \pi^*$		−1.20 (120)
	362 (16 700)	d $\rightarrow \pi^*$		
	378 (22 700)	d $\rightarrow \pi^*$		
17 *fac*-[Re^I(biq)(CO)$_3$(ISNA)]PF$_6$	268 (46 300)	$\pi \rightarrow \pi^*$		−0.68 (65)
	308sh (13 900)	$\pi \rightarrow \pi^*$		−1.26 (80)
	360 (19 100)	d $\rightarrow \pi^*$		
	378 (26 800)	d $\rightarrow \pi^*$		
18 *trans,fac*-[Ru^{II}Cl(pdma)$_2${4,4′-bpy-*N*-(C$_2$H$_4$NHCO-4-C$_5$H$_4$N)}Re^I(biq)(CO)$_3$](PF$_6$)$_3$	270 (80 000)	$\pi \rightarrow \pi^*$	1.17 (60)	−0.67 (70)
	362 (21 900)	d $\rightarrow \pi^*$(biq)		−1.27 (75)
	378 (29 600)	d $\rightarrow \pi^*$(biq)		
	498 (8200)	d $\rightarrow \pi^*$(4,4′-bpy)		
19 *trans,fac*-[Ru^{II}Cl(pdma)$_2${bpe-*N*-(C$_2$H$_4$NHCO-4-C$_5$H$_4$N)}Re^I(biq)(CO)$_3$](PF$_6$)$_3$	272 (51 600)	$\pi \rightarrow \pi^*$	1.13 (70)	−0.62 (60)
	306 (39 200)	$\pi \rightarrow \pi^*$(C=C)		−1.15 (100)
	362 (19 300)	d $\rightarrow \pi^*$(biq)		
	378 (25 400)	d $\rightarrow \pi^*$(biq)		
	504 (12 200)	d $\rightarrow \pi^*$(bpe)		

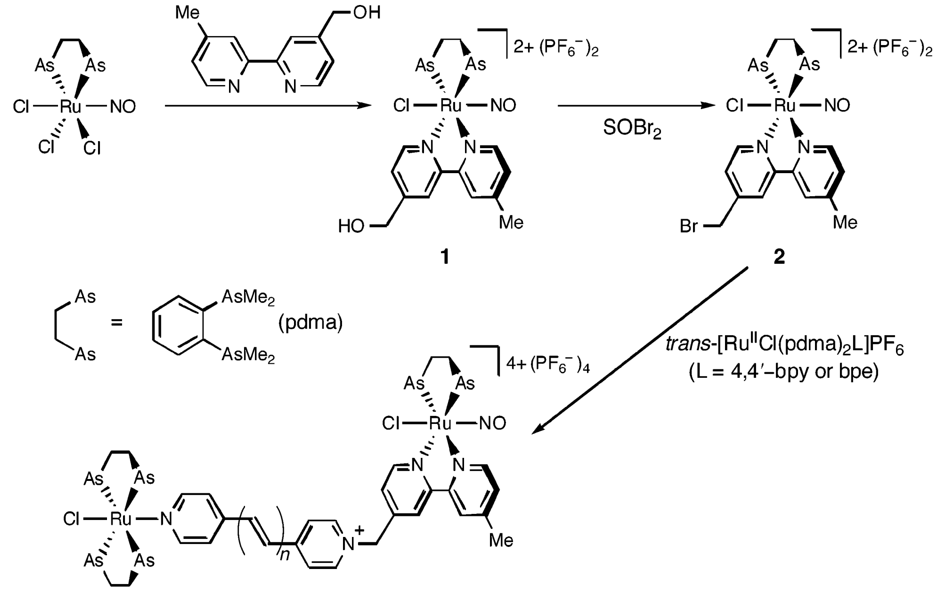
[a] Solutions ca. 3−8 × 10^{-5} M. [b] Measured in solutions ca. 10^{-3} M in analyte and 0.1 M in [NBu$^n_4$]PF$_6$ at a Pt disk working electrode with a scan rate of 200 mV s^{-1}. Ferrocene internal reference $E_{1/2} = 0.45$ V, $\Delta E_p = 60-70$ mV. [c] Data taken in part from ref 13. [d] E_{pc} for an irreversible reduction process. [e] Data taken from ref 11. [f] Data taken from ref 12. [g] E_{pa} for an irreversible oxidation process.

Table 2. Crystallographic Data and Refinement Details for Complex Salts 5·CHCl$_3$, 8, 9·Me$_2$CO, 16, and 17D·3MeCN

	5·CHCl$_3$	**8**	**9**·Me$_2$CO	**16**	**17D**·3MeCN
formula	$C_{25}H_{16}Cl_3F_3N_3O_6ReS$	$C_{27}H_{18}BrF_6N_3O_3PRe$	$C_{31}H_{25}F_6N_3O_6PRe$	$C_{30}H_{21}F_3N_3O_8ReS$	$C_{60}H_{42}F_6N_9O_{10}PRe_2$
M	836.02	843.52	866.71	826.76	1566.40
cryst syst	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	8.798(5)	11.4905(2)	13.4828(16)	10.529(6)	13.3162(11)
b/Å	12.597(5)	12.8508(2)	14.1333(9)	12.626(7)	14.6911(12)
c/Å	14.237(5)	19.4117(4)	16.697(3)	13.129(12)	16.745(2)
α/deg	113.314(5)			101.79(6)	64.772(8)
β/deg	92.841(5)	107.22	102.100(13)	106.89(7)	85.426(9)
γ/deg	92.544(5)			92.26(6)	84.519(5)
U/Å^3	1443.7(11)	2737.95(9)	3111.1(7)	1626(2)	2947.1(5)
Z	2	4	4	2	2
T/K	293(2)	120(2)	120(2)	120(2)	120(2)
μ/mm^{-1}	4.623	6.033	4.043	3.871	4.217
cryst size/mm	0.2 × 0.1 × 0.08	0.10 × 0.04 × 0.01	0.38 × 0.32 × 0.18	0.24 × 0.11 × 0.09	0.40 × 0.40 × 0.20
no. of reflns collected	21 088	41 479	39 149	32 283	65 654
no. of indep reflns (R_{int})	5082 (0.0575)	6205 (0.1787)	7126 (0.0493)	7397 (0.0755)	13 208 (0.0292)
goodness-of-fit on F^2	1.064	1.045	1.022	1.019	1.041
final R1, wR2 [$I > 2\sigma(I)$]^a	0.0274, 0.0697	0.0451, 0.1147	0.0245, 0.0593	0.0515, 0.1196	0.0228, 0.0519
(all data)	0.0287, 0.0704	0.0517, 0.1199	0.0375, 0.0647	0.0772, 0.1275	0.0278, 0.0539

[a] The structures were refined on F_o^2 using all data; the values of R1 are given for comparison with older refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$.

Scheme 1. Syntheses of the Diruthenium Complex Salts 10 and 11



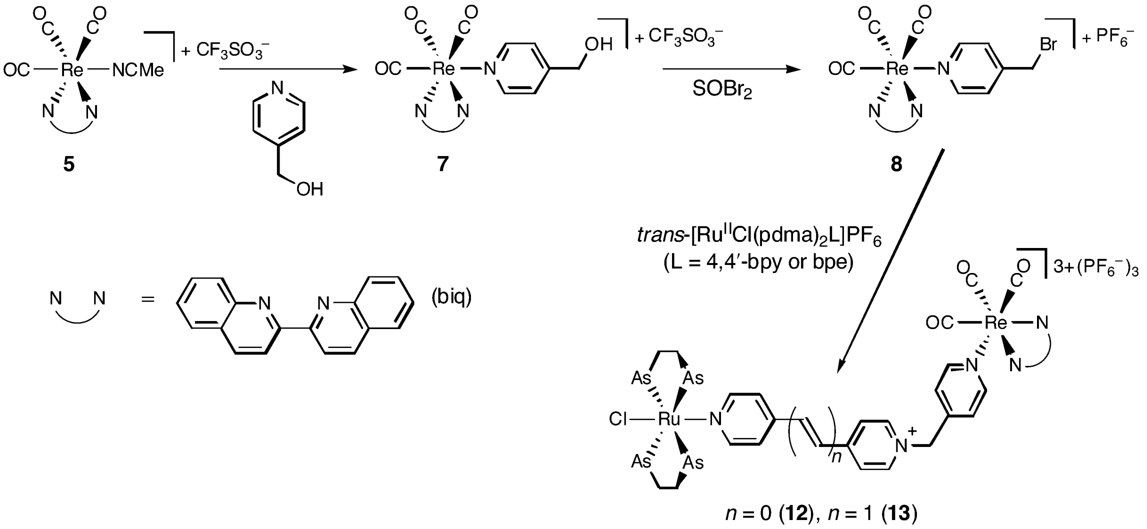
n = 0 (**10**), *n* = 1 (**11**)

hydrogen atoms included in idealized positions with thermal parameters riding on those of the parent atom. Crystallographic data and refinement details are presented in Table 2.

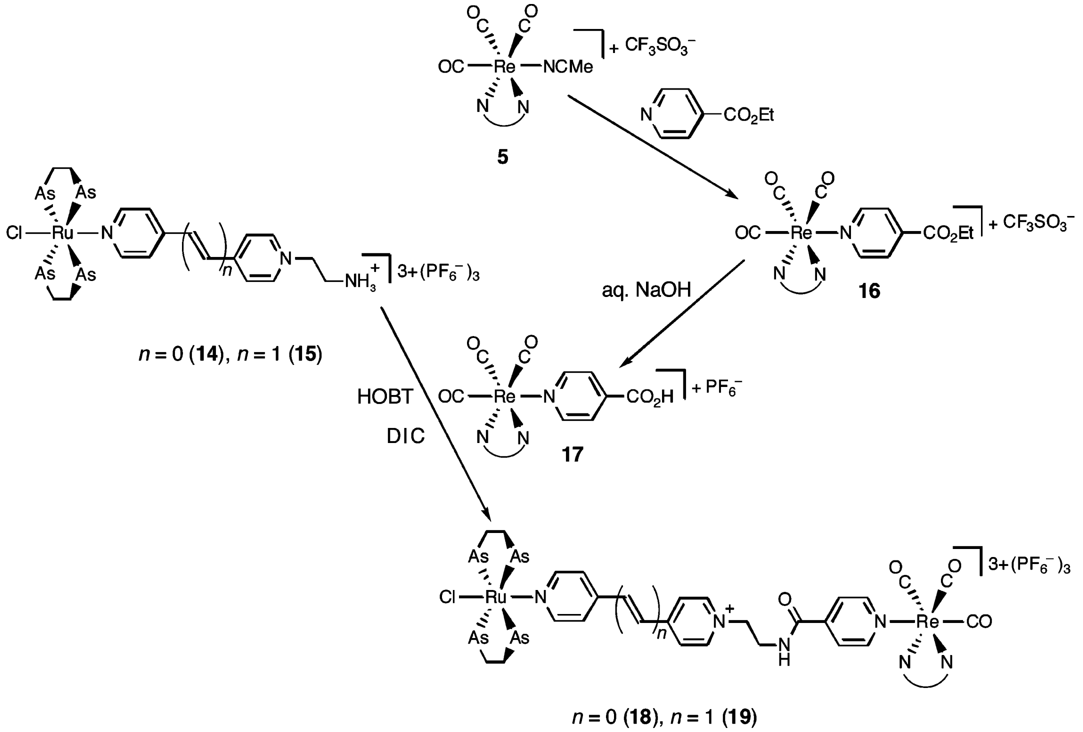
Results and Discussion

Syntheses and Characterization. We have prepared the homonuclear bimetallic complex salts **10** and **11** by nucleophilic substitution reactions between *trans*-[Ru^{II}Cl(pdma)$_2$L]$^+$ (L = 4,4′-bpy or bpe)[18] and the new bromomethyl complex in **2** (Scheme 1). We have also prepared the related heteronuclear bimetallics **12** and **13** via a similar methodology (Scheme 2). Although the Re^I precursor complex **4** and salt **5** have been reported previously,[24,25] full details were not given, so we include these procedures and data here. All of these coupling reactions proceed slowly at room temperature in DMF in the presence of AgCF$_3$SO$_3$. Although the use of Ag^I salts to labilize bromide ions toward substitution is very common, in these reactions the anion also seems to play an important role and the use of AgBF$_4$ in place of AgCF$_3$SO$_3$ results in lower yields. This may be because the presence of a less coordinating anion such as BF$_4^-$ causes the formation of an unstable carbocation, which can decompose before it reacts. Attempts to improve the efficiencies of these coupling reactions by heating or using catalytic amounts of KI in place of the silver salt resulted in the formation of side products. The isolated yields of **10**−**13** (obtained as PF$_6^-$ salts after column chromatographic purification) are ca. 30%, and the faster reactions with *trans*-[Ru^{II}Cl(pdma)$_2$(bpe)]$^+$ may be due to increased basicity of the uncoordinated pyridyl nitrogen atom arising from the mildly electron-donating ability of the 4-ethylene unit.

Scheme 2. Syntheses of the Ruthenium−Rhenium Complex Salts 12 and 13



Scheme 3. Syntheses of the Ruthenium-Rhenium Complex Salts 18 and 19



Because it seems likely that these substitution reactions may proceed via the formation of triflatomethyl intermediates, we have attempted to isolate such complexes by treatment of **2** or **8** with AgCF$_3$SO$_3$ in DMF in the absence of another nucleophilic species. Surprisingly, these reactions resulted in the formation in high yields of the formyloxy derivatives **3** and **9** (Figure 1), rather than the expected triflato derivatives. Although unusual, there is literature precedent for the conversion of (albeit noncomplexed) alkyl bromides to alkyl formates by treatment with Ag^I salts in the presence of DMF.[32] We have not observed any evidence for the formation of **3** or **9** in the presence of *trans*-[Ru^{II}Cl(pdma)$_2$L]$^+$ (L = 4,4′-bpy or bpe). All of the new complex salts **1**−**3** and **6**−**13** show diagnostic ^{1}H NMR spectra, and mass spectra (in most cases) and elemental analyses provide further confirmation of identity and purity. Interestingly, the 4,4′-bpy-bridged complexs in **10** and **12** show reasonable +FAB mass spectra, while their bpe-containing analogues in **11** and **13** do not, despite repeated attempts.

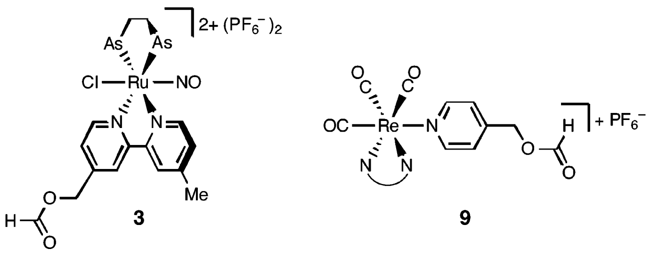


Figure 1. Structures of the formyloxy complex salts **3** and **9** (see Schemes 1 and 2 for structural abbreviations).

The heteronuclear bimetallic complexes in **18** and **19** were prepared in reasonable yields via amide coupling reactions (Scheme 3). A portion of a representative ^{1}H NMR spectrum of **19** is shown in Figure 2. The pendent amino complexes in **14** and **15** are isolated as their HPF$_6$ adducts when reprecipitated

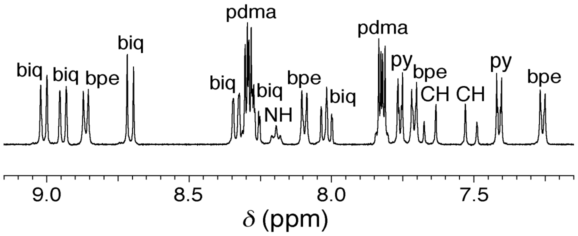


Figure 2. Aromatic region of the ^{1}H NMR spectrum of the heteronuclear bimetallic complex salt **19** recorded at 400 MHz in acetone-d_6 at 293 K (py = pyridyl).

by using aqueous NH_4PF_6, and ^{1}H NMR spectra revealed trace impurities in some samples of these compounds that could not be removed via reprecipitations or silica gel column chromatography. However, only satisfactorily pure samples of **14** and **15** were used in the syntheses of **18** and **19**. The carboxyl-functionalized complex in **17** was prepared via its ester precursor primarily because the poor solubility of isonicotinic acid (ISNA) precludes a direct synthesis from *fac*-[Re^I(2,2′-biq)(CO)$_3$-(MeCN)]CF_3SO_3, but this approach also avoids any possibility of competitive carboxylate complexation. When compared with **12** and **13**, the presence of a longer flexible spacer between the electron-accepting groups is expected to influence the photophysical properties of **18** and **19**, and in particular the increased distance between the terminal D and A groups is intended to prolong PICS lifetimes. Although the greater flexibility may allow these groups to approach each other more closely, this factor may be offset by mutual electrostatic repulsion between the cationic complex units.

Electronic Spectroscopy Studies. The UV−visible absorption spectra of compounds **1**−**19** have been measured in acetonitrile, and the results are presented in Table 1, together with data for some reference complex salts. The previously reported *trans*-[Ru^{II}Cl(pdma)(2,2′-bpy)(NO)]$(PF_6)_2$[13] and the related complexes in **1**−**3** exhibit d(Ru^{II}) → π*(2,2′-bpy) MLCT transitions at relatively high energies in the near-UV region (at ca. 320 nm), rendering these compounds almost colorless. Additional intense absorptions to higher energies are attributable to π → π* intraligand transitions.

The mononuclear Re^I complexes in **5**−**9**, **16**, and **17** all exhibit two relatively sharp absorptions in the region ca. 360−380 nm, which are assigned to d(Re^I) → π*(biq) MLCT transitions, by analogy with previous studies on related complexes.[14,33] For the known precursor complex **4**,[24] these bands are shifted to slightly higher energies, and an additional weak but distinct absorption is observed at 426 nm. In dichloromethane solution, **4** gives bands at 375, 438, and 481 nm (shoulder), and shifting of the low-energy band to higher energy with increasing solvent polarity has been noted, leading to an assigment of d(Re^I) → π*(biq) MLCT for this weak absorption.[24] For complex salt **5**, the MLCT absorption has been reported as a shoulder at 430 nm,[25] but we have been unable to reproduce this result.

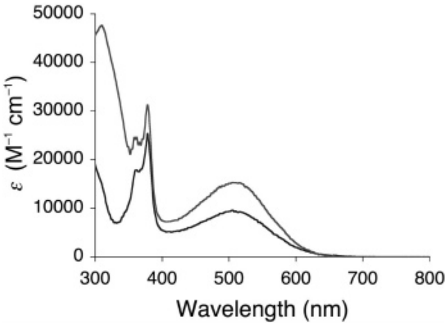


Figure 3. UV−visible absorption spectra of the heteronuclear bimetallic complex salts **12** (lower trace) and **13** (upper trace) in acetonitrile at 293 K.

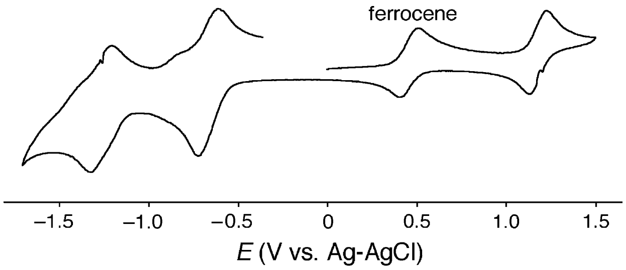


Figure 4. Cyclic voltammogram of the heteronuclear bimetallic complex salt **18** at a scan rate of 200 mV s^{-1} in acetonitrile at 293 K.

The bimetallic complexes in **10**−**13** all show a single broad absorption at ca. 510 nm, which are assigned to d(Ru^{II}) → π*-(4,4′-bpy/bpe) MLCT transitions. These absorptions are found to somewhat lower energies when compared with the corresponding bands in the monometallic reference compounds *trans*-[Ru^{II}Cl(pdma)$_2$(MeQ$^+$)]$(PF_6)_2$[11] and *trans*-[Ru^{II}Cl(pdma)$_2$-(Mebpe$^+$)]$(PF_6)_2$;[12] this observation is consistent with the greater electron-withdrawing ability of a 4-CH_2-4′-Me-2,2′-bpy or 4-$CH_2C_5H_4N$ unit as opposed to a methyl substituent. These low-energy MLCT absorptions are also significantly more intense in the bpe-containing complexes in **11** and **13**, a result of increased π-orbital overlap due to greater coplanarity of the pyridyl rings when compared with the analogous 4,4′-bpy-containing species in **10** and **12**. Each of the Ru^{II}−Re^I complexes in **12** and **13** also shows two intense absorptions in the region ca. 360−380 nm, which are assigned to d(Re^I) → π*(biq) MLCT transitions, together with high-energy intraligand π → π* bands. Representative absorption spectra of these compounds are shown in Figure 3.

The pendent amino complexes in **14** and **15** display d(Ru^{II}) → π*(4,4′-bpy/bpe) MLCT bands that are only very slightly red-shifted when compared with those of the monometallic MeQ$^+$ or Mebpe$^+$ reference complexes.[11,12] As expected, the absorption spectra of the Ru^{II}−Re^I complexes in **18** and **19** resemble closely those of **12** and **13**, but the lowest energy MLCT bands are found to slightly higher energies in the former, suggesting that a Re^I-coordinated 4-$CH_2C_5H_4N$ unit is slightly more electron withdrawing than its amide-containing counterpart. The pairs **14**/**15** and **18**/**19** also show the hyperchromic effect on the visible MLCT bands of increased π-orbital overlap in the bpe-containing species, as noted above for **10**/**11** and **12**/**13**. The close similarities between the MLCT spectra for **10**−**13**, **18**, and **19** and those of the related monometallic complexes show that only relatively weak ground-state electronic interactions occur in the bimetallic assemblies. This observation is consistent with the relatively large D−A separations and

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(33) Howell, S. L.; Scott, S. M.; Flood, A. H.; Gordon, K. C. *J. Phys. Chem. A* **2005**, *109*, 3745.

(34) See for example: (a) Ford, P. C.; Bourassa, J.; Miranda, K.; Lee, B.; Lorkovic, I.; Boggs, S.; Kudo, S.; Laverman, L. *Coord. Chem. Rev.* **1998**, *171*, 185. (b) Ford, P. C.; Wecksler, S. *Coord. Chem. Rev.* **2005**, *249*, 1382.

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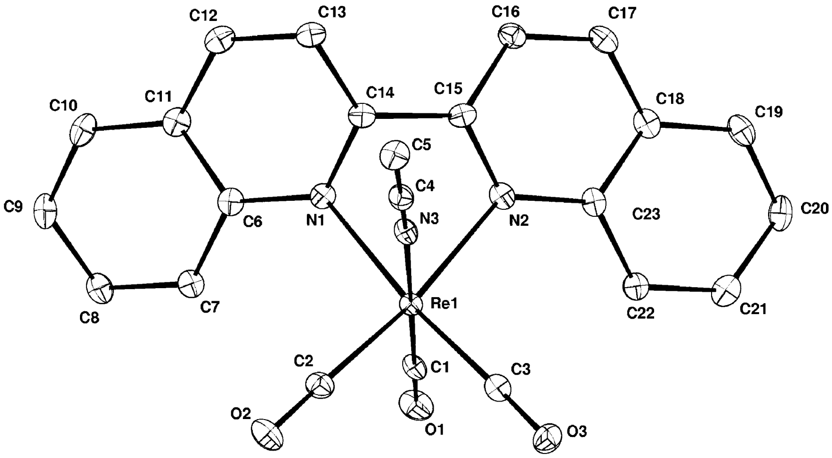

Figure 5. Representation of the molecular structure of the complex cation in the salt **5**·$CHCl_3$, with hydrogen atoms omitted for clarity (50% probability ellipsoids).

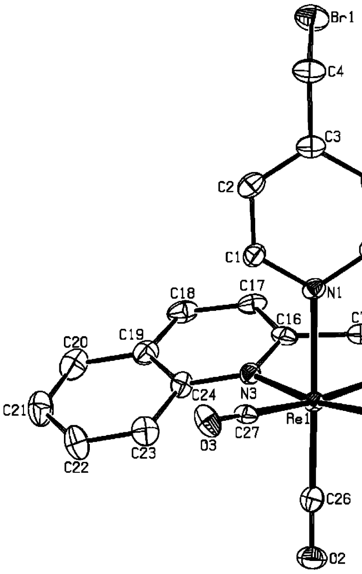

Figure 6. Representation of the molecular structure of the complex cation in the salt **8**, with hydrogen atoms omitted for clarity (50% probability ellipsoids).

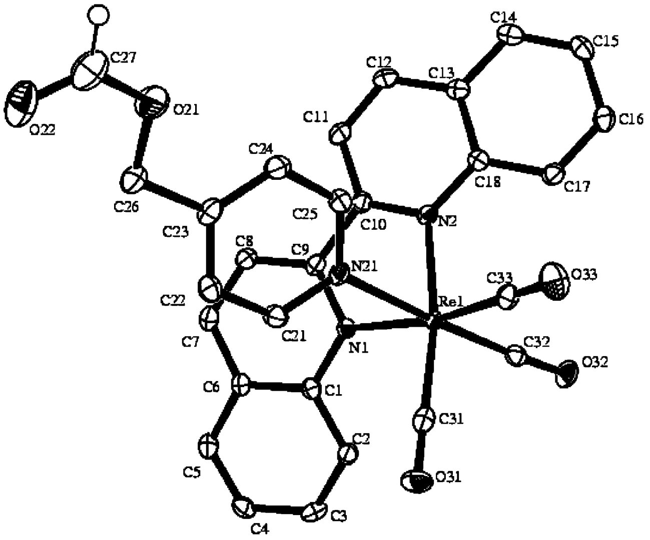

Figure 7. Representation of the molecular structure of the complex cation in the salt **9**·Me_2CO, with hydrogen atoms (except that on the formyl carbon) omitted for clarity (50% probability ellipsoids).

especially the presence of saturated CH_2 linkages between the chromophoric centers.

Infrared Spectroscopy Studies. The new complexes show intense and diagnostic infrared absorption bands, confirming the presence of linearly coordinated carbonyl (in **7**−**9**, **12**, **13**, **16**−**19**) or nitrosyl (in **1**−**3**, **10**, **11**) ligands. As mentioned previously, the presence of such ligands in the A units is intended to render the bimetallic complexes in **10**−**13**, **18**, and **19** ideally suited to study via TRIR spectroscopy. However, although this technique has often been applied successfully to *fac*-$\{Re^I(2,2'\text{-bpy})(CO)_3\}^+$-containing and closely related complexes,[15a−m] we are not aware of any precedent for similar studies with metal nitrosyl species. If electron transfer occurs to the terminal A unit, then this will cause an increase in electron density around the Ru^{II}-nitrosyl or Re^I-carbonyl center. A greater extent of π-back-bonding to the NO or CO ligands will result, and the IR absorptions should therefore display low-energy shifts. The results of ultrafast TRIR and other time-resolved spectroscopic studies will be reported in a subsequent publication.

Given the context of this work, some comments on the thermal and photochemical stabilities of the new complexes are clearly appropriate. Their overall stability is reasonable, but a degree of photosensitivity is evident for solutions of the pdma-containing species in coordinating solvents such as acetonitrile, and this appears to be attributable to photolysis of the axial Ru−pyridyl bond of the electron-donating *trans*-$\{Ru^{II}Cl(\text{pdma})_2\}^+$ centers. This instability is not severe enough to preclude the requisite time-resolved spectroscopic studies that will be used to probe the formation of PICS states, but could obviously limit any practical applications of our complex assemblies. However, it should be remembered that photostability may change considerably at lower temperatures and/or under conditions of surface/matrix confinement. Furthermore, the particular compounds prepared are merely first-generation models designed for fundamental photoexcitation studies and as such are not realistically expected to find practical applications themselves, but rather to provide information that may be used to guide future studies.

Electrochemical Studies. All of the compounds **1**−**19** have been studied by cyclic voltammetry in acetonitrile, and the results are presented in Table 1, together with data for some reference complex salts. A representative voltammogram of **18** is shown in Figure 4.

The reference complex in *trans*-$[Ru^{II}Cl(\text{pdma})(NO)(2,2'\text{-bpy})](PF_6)_2$ and the related mononuclear species **1**−**3** exhibit quasi-reversible waves in the region ca. 0.1−0.2 V vs Ag−AgCl,

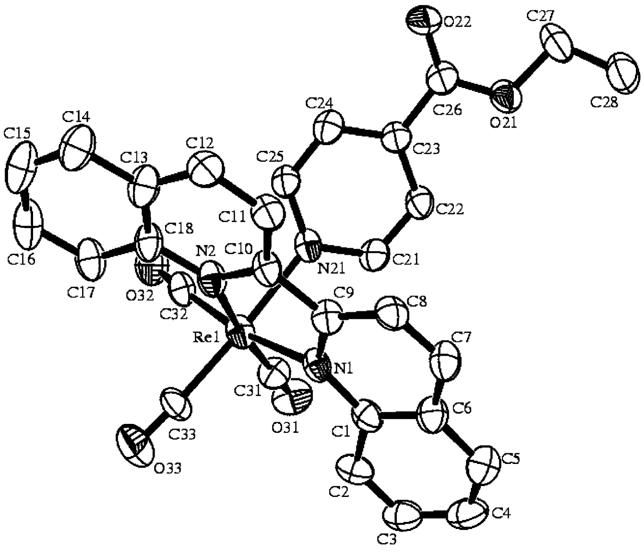

Figure 8. Representation of the molecular structure of the complex cation in the salt **16**, with hydrogen atoms omitted for clarity (50% probability ellipsoids).

assigned to one-electron reductions of the $\{\mathrm{Ru^{II}(NO)}\}^{3+}$ centers. Similar processes are also observed for the homonuclear bimetallic complexes in **10** and **11**. In addition, totally irreversible processes occur at lower potentials in *trans*-$[\mathrm{Ru^{II}Cl(pdma)(NO)(2,2'\text{-}bpy)}](\mathrm{PF_6})_2$ and **1**−**3**, presumably attributable to reductions of the bpy ligands. The mononuclear $\mathrm{Re^I}$ compounds **4**−**7**, **9**, **16**, and **17** all show reversible waves associated with one-electron reductions of the biq ligand;[14] in the case of **8**, the complete irreversibility of this process may be attributed to the presence of a reactive bromomethyl substituent. This reduction occurs at a potential that is lower by ca. 200 mV for complex **4** than for **5**−**9**, **16**, or **17**, which may be ascribed to the greater electron-donating ability of the chloride co-ligand when compared with acetonitrile or a pyridyl derivative. The $\mathrm{biq}^{0/-}$ reduction potential is completely insensitive to the 4-substituents on the pyridyl ligand. With the exception of complex **4**, further $\mathrm{biq}^{-/2-}$ reduction processes[14] are also observed, which are truly reversible only in the cases of **6**, **7**, and **17** and quasi-reversible for **16**. The irreversible oxidation wave in **4** is most reasonably assigned to a $\mathrm{Re^{II/I}}$ process;[14] we have not observed similar waves in any of the other compounds, but these may be obscured by the solvent background. The origin of the irreversible oxidation in **8** is unclear.

The complex in salt **14** exhibits two reversible reduction processes, attributable to the 4,4′-bpy unit. However, an unexplained shoulder is also observed before the first cathodic peak. As also observed in the model complex *trans*-$[\mathrm{Ru^{II}Cl(pdma)_2(Mebpe^+)}]^{2+}$,[12] the introduction of the ethylene bridge in **15** leads to less well-defined reductive electrochemical behavior.

All of the bimetallic complexes in **10**−**13**, **18**, and **19** exhibit reversible $\mathrm{Ru^{III/II}}$ oxidation waves at ca. 1.1−1.2 V vs Ag−AgCl, attributable to the *trans*-$\{\mathrm{Ru^{II}Cl(pdma)_2}\}^+$ centers. The complexes in **10**−**13** also exhibit unresolvable manifolds of overlapping waves at negative potentials, unfortunately meaning that firm conclusions concerning the thermodynamic likelihood of PICS cannot be drawn. However, it can be inferred from the reduction behavior of the mononuclear species *trans*-$[\mathrm{Ru^{II}Cl(pdma)_2L}]^{2+}$ ($\mathrm{L = MeQ^+}$ or $\mathrm{Mebpe^+}$), **1** and **7**, that the driving forces for secondary electron transfer from the pyridinium unit to the terminal $\{\mathrm{Ru^{II}(NO)}\}^{3+}$ or *fac*-$\{\mathrm{Re^I(biq)(CO)_3}\}^+$ moieties are ca. 0.9 eV in the case of **10** and **11** and ca. 0.1 eV for **12** and **13**. The amide-bridged bimetallic complexes in **18** and **19** appear to exhibit two quasi-reversible reduction processes at potentials similar to those observed for the monometallic $\mathrm{Ru^{II}}$ and $\mathrm{Re^I}$ complexes. However, the relative peak currents of these waves when compared with those of the $\mathrm{Ru^{III/II}}$ waves show that the former arise from overlapping processes (Figure 4). Although it is therefore again not possible to comment with any confidence on the thermodynamic likelihood of PICS, the data for the constituent mononuclear complexes suggest that modest driving forces should exist.

Crystallographic Studies. Single-crystal X-ray structures have been obtained for the complex salts $\mathbf{5}\cdot\mathrm{CHCl_3}$, **8**, $\mathbf{9}\cdot\mathrm{Me_2}$-

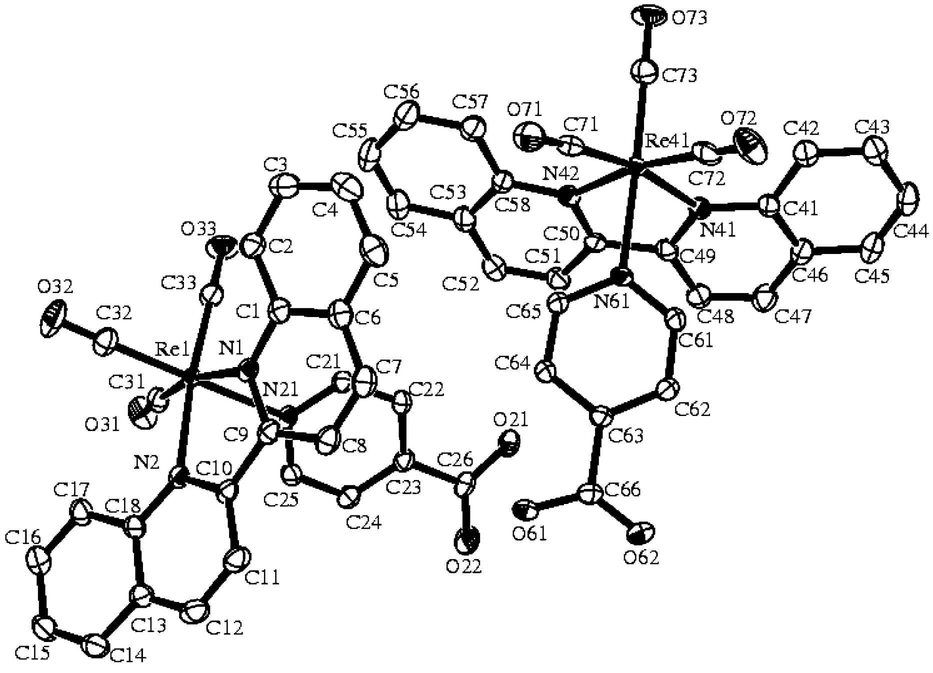

Figure 9. Representation of the molecular structure of the two inequivalent complex cations in the salt $\mathbf{17D}\cdot3\mathrm{MeCN}$, with hydrogen atoms omitted for clarity (50% probability ellipsoids).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Complex Salts 5·$CHCl_3$, 8, 9·Me_2CO, 16, and 17D·3MeCN (two inequivalent complex cations)

	5·$CHCl_3$	**8**	**9**·Me_2CO	**16**	**17D**·3MeCN	
Re−N(biq)	2.192(3)	2.203(5)	2.178(2)	2.171(5)	2.196(2)	2.191(2)
Re−N(biq)	2.210(4)	2.180(5)	2.182(2)	2.186(5)	2.196(2)	2.194(2)
Re−N(L)[a]	2.152(4)	2.222(5)	2.216(2)	2.198(5)	2.201(2)	2.211(2)
Re−C(trans-biq)	1.931(4)	1.925(6)	1.920(3)	1.897(6)	1.914(3)	1.917(3)
Re−C(trans-biq)	1.941(4)	1.925(6)	1.920(3)	1.941(8)	1.922(3)	1.918(3)
Re−C(trans-L)	1.926(4)	1.925(6)	1.919(3)	1.929(6)	1.923(3)	1.935(3)
N(biq)−Re−N(biq)	74.20(13)	74.59(17)	74.04(8)	74.08(19)	74.06(8)	74.58(8)
N(biq)−Re−N(L)	82.58(13)	83.14(17)	80.22(8)	82.00(18)	84.26(8)	82.69(8)
N(biq)−Re−N(L)	84.27(13)	82.26(16)	82.85(8)	82.11(18)	79.76(8)	80.77(8)
N(biq)−Re−C(trans-biq)	171.96(15)	173.9(2)	170.83(10)	170.3(2)	173.69(10)	169.17(10)
N(biq)−Re−C(trans-biq)	98.97(16)	98.9(2)	97.59(10)	100.8(2)	101.37(10)	97.78(11)
N(biq)−Re−C(trans-biq)	171.45(15)	171.0(2)	169.25(11)	173.0(2)	167.31(10)	170.33(11)
N(biq)−Re−C(trans-biq)	100.43(15)	102.2(2)	99.56(10)	100.1(2)	99.26(10)	100.40(10)
N(biq)−Re−C(trans-L)	96.12(15)	96.3(2)	102.38(10)	98.0(2)	100.19(10)	98.05(10)
N(biq)−Re−C(trans-L)	94.97(14)	95.9(2)	96.30(10)	93.4(2)	96.27(10)	97.36(11)
N(L)−Re−C(trans-biq)	89.80(16)	90.8(2)	92.12(10)	93.5(2)	90.68(10)	87.05(10)
N(L)−Re−C(trans-biq)	91.01(15)	91.3(2)	90.51(10)	89.1(2)	88.94(10)	92.50(10)
N(L)−Re−C(trans-L)	178.63(14)	178.2(2)	176.96(9)	175.2(2)	179.43(11)	177.75(10)
C(trans-biq)−Re−C(trans-biq)	85.79(18)	83.7(2)	88.12(11)	84.4(3)	84.37(12)	86.09(12)
C(trans-biq)−Re−C(trans-L)	90.83(17)	91.0(2)	89.10(11)	91.1(3)	88.77(12)	92.08(12)
C(trans-biq)−Re−C(trans-L)	90.25(17)	89.1(2)	86.75(12)	90.4(3)	91.17(12)	89.51(12)
dihedral angle 1[b]	21.45(4)	16.73(0.14)	15.94(8)	10.2(2)	12.77(9)	13.10(8)
dihedral angle 2[c]	39.20(6)	36.64(0.18)	42.40(10)	40.2(3)	39.12(12)	42.17(12)

[a] L = acetonitrile or pyridyl ligand. [b] Between the planes of the two quinolinyl rings. [c] Between the planes defined by the equatorial *cis*-$\{Re^I(CO)_2\}^+$ unit and the C−N−C−C−N−C chain of the biq ligand.

CO, **16**, and *fac*-$[Re^I(biq)(CO)_3(NC_5H_4CO_2)]_2$·$HPF_6$·3MeCN (**17D**·3MeCN, derived from **17**). Representations of the molecular structures are shown in Figures 5−9, and selected interatomic distances and angles are presented in Table 3. To our knowledge, the only previously reported closely related crystal structure is that containing a *fac*-$\{Re^IBr(CO)_3\}^+$ moiety coordinated to a biq ligand with a propyl linkage between its 3 and 3′ positions.[19] In **17D**·3MeCN, the carboxylate group forms a strong hydrogen bond with a symmetry-related molecule using only one hydrogen atom, leading to a charge of only +1 over the two complex units, rather than +2. This result is reproducible and further supported by elemental analyses of the dried crystalline material (Found: C, 44.81; H, 2.16; N, 5.76. Calc for $C_{54}H_{33}F_6N_6O_{10}PRe_2$: C, 44.94; H, 2.30; N, 5.82).

All of the complexes show an essentially octahedral geometry about the rhenium ion with the usual facial arrangement of the carbonyl ligands. In **5**·$CHCl_3$, the Re−N(MeCN) distance is ca. 0.05 Å shorter than the Re−N(biq) distances, largely attributable to more extensive π-back-bonding to the acetonitrile ligand. No clear differences between the Re−N(biq) and Re−N distances are evident in **8**, **16**, and **17D**·3MeCN, but in **9**·Me_2CO the Re−N(pyridyl) distance is ca. 0.04 Å longer than the Re−N(biq) distances, indicating that the 4-(formyloxymethyl)-pyridyl ligand is a weaker π-acceptor than biq. The three Re−C distances are very similar in all of the complexes. The biq ligands are not fully planar, but display some degree of bowing about the central C−C bond. These ligands are also tilted considerably out of the equatorial plane defined by the Re^I ion and the trans carbonyl ligands, toward the acetonitrile or pyridyl ligand (Table 3). For example, in **8** the angle between the planes of the two quinolinyl rings is ca. 17°, and the angle between the planes defined by Re1/C25/O1/C27/O3 and C15/N2/C7/C16/N3/C24 is ca. 37°.

Conclusion

We have synthesized six new Ru^{II} and Re^I bimetallic CQ assemblies designed to display long-lived photoinduced charge-separated states, together with a number of monometallic precursor complexes. The UV−visible absorption spectra of the bimetallic species indicate the presence of only limited ground-state electronic interactions between the MLCT chromophoric units, and cyclic voltammetric studies provide evidence that these assemblies contain thermodynamic driving forces for charge separation. The monometallic *fac*-$\{Re^I(biq)(CO)_3\}^+$-containing complex salts show excellent crystallization behavior, and five single-crystal X-ray structures have been determined. The photoexcitation properties of the new CQ complex assemblies will be investigated by using ultrafast TRIR experiments and also complementary transient resonance Raman measurements, and the results will be reported in a future publication.

Acknowledgment. We thank the EPSRC for support (grant GR/R81459 and a Ph.D. studentship for E.C.F.).

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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